Long wave theory for experimental devices with compressed/expanded surfactant monolayers

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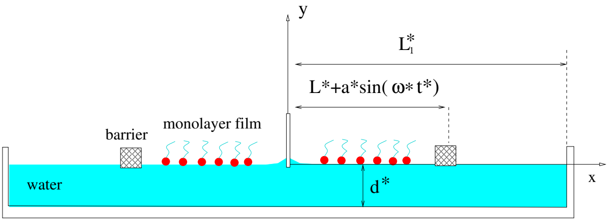
Experiments:

1. H.Hilles, F. Monroy,L. Bonales, F. Ortega, R.G. Rubio, Fourier-transform rheology of polymer Langmuir monolayers: analysis of the non-linear and plastic behaviors. *Adv. Colloid Interface* (2006).
2. H. Hilles, A. Maestro, F. Monroy, F. Ortega, R.G. Rubio, Polymer monolayers with a small viscoelastic linear regime: Equilibrium and rheology of poly(octadecyl acrylate) and poly(vinyl stearate) *J. Chem. Phys.* (2007).
3. N. Mitsui, T. Morioka, M. Kawaguchi, Surface dilational moduli of poly(vinyl acetate), poly(methyl methacrylate), and their blend films spread at the airâwater interface.*Colloids Surf., A* (2012).
4. T. Kobayashi, M. Kawaguchi, Surface dilational moduli of latex-particle monolayers spread at air-water interface. J. Colloid Interface Sci. (2013).

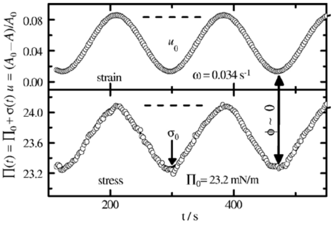


1. The distance between the two solid barriers varies harmonically with amplitude a^* and frequency ω^*, around a mean value $2L^*$.
2. $d^* << L^* \sim L_1^*$.
3. The surfactant is spread initially on the free surface between the barriers and let to relax to spatially uniform state before initiating the motion of the barriers.
4. All subsequent states of the system are independent of the transversal coordinate, obtaining a two dimensional formulation.

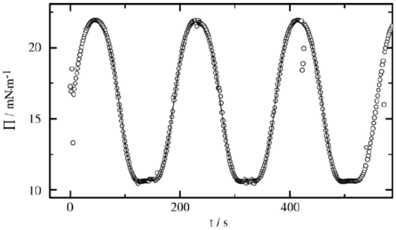
Experiment by Hilles et al. (2006).

Results for a monolayer of Poly(vinyl acetate) (PVAc).

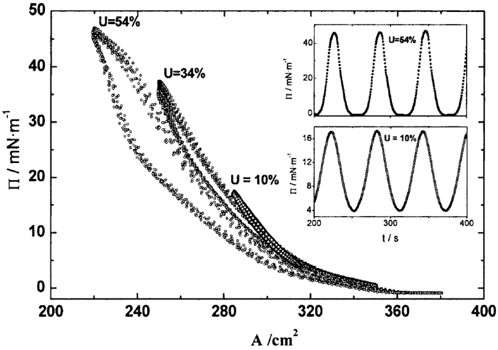
a) Strain amplitude 8 % and $\omega^* = 0{,}034$Hz



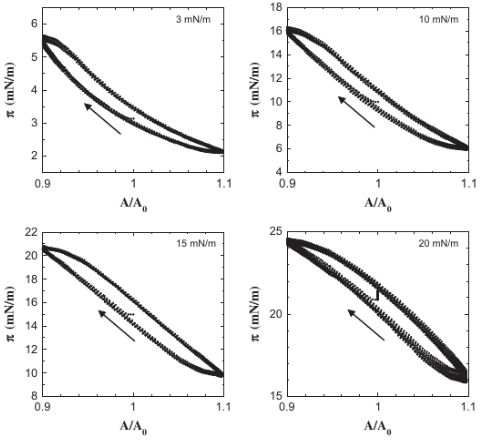
b) Strain amplitude 37 % and $\omega^* = 0{,}005$Hz



• **Lissajous orbits.** Hysteresis cycles for PODA monolayers for different values of the strain indicate that the process (compression/expansion) is typically irreversible.



• **Typical Lissajous orbits** for different initial conditions, measured at fixed strain 10 % and frequency 0,01Hz.



SCALING AND NONDIMENSIONALIZATION

1. $d^*,\ 1/\omega^*,\ \mu/(\rho d^*),\ \mu^2/(\rho d^{*2})$, and c_0^*.
2. $(x, y) = (x^*, y^*)/d^*,\ f = f^*/d^*,\ (L, L_1, a) = (L^*, L_1^*, a^*)/d^*$.
3. $t = \omega^* t^*,\ (u, v) = \rho d^*(u^*, v^*)/\mu,\ p = \rho d^{*2} p^*/\mu^2$.
4. $c = c^*/c_0^*$.

Nondimensional continuity and Navier-Stokes equations

$$\partial_x u + \partial_y v = 0,$$
$$\omega \partial_t u + u \partial_x u + v \partial_y u = -\partial_x p + \partial^2_{xx} u + \partial^2_{yy} u,$$
$$\omega \partial_t v + u \partial_x v + v \partial_y v = -\partial_y p + \partial^2_{xx} v + \partial^2_{yy} v.$$

These equations apply in the spatial region

$$-LX_b(t) < x < LX_b(t), \quad -1 < y < f,$$

where, for periodic compression/expansion,

$X_b(t) = 1 + a \sin t$ with $t > 0$ and $0 < a < 1$.

Formulation

Boundary conditions

- At the bottom of the container: $u = v = 0$ at $y = -1$.
- At the free surface, $y = f$:

$$
\begin{aligned}
&\omega\partial_t f + u\partial_x f = v,\\
&\partial_y u + \partial_x v + [2\partial_y v - 2\partial_x u - (\partial_y u + \partial_x v)\partial_x f]\partial_x f =\\
&\qquad -\mathcal{P}\partial_x \Pi(c)/\sqrt{1+|\partial_x f|^2},\\
&p - \mathcal{G} f + \partial_x\left[\frac{[\mathcal{S} - \mathcal{P}\Pi(c)]\partial_x f}{(1+|\partial_x f|^2)^{1/2}}\right] =\\
&\qquad 2\frac{\partial_y v - (\partial_y u + \partial_x v)\partial_x f + \partial_x u(\partial_x f)^2}{1+|\partial_x f|^2},\\
&\omega\partial_t[\sqrt{1+|\partial_x f|^2}\, c] + \partial_x[(u - v\partial_x f)c] = \mathcal{D}\partial_x\left[\frac{D(c)\partial_x c}{\sqrt{1+|\partial_x f|^2}}\right],
\end{aligned}
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\end{aligned}
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NONDIMENSIONAL PARAMETERS OF THE PROBLEM

- $\omega = \rho d^{*2}\omega^*$, $\mathcal{G} = \rho^2 g d^{*3}/\mu^2$, $\mathcal{S} = \rho\sigma_0 d^*/\mu^2$.
- $\mathcal{P} = \rho^* d^* \Pi^*(c_0^*)/\mu^2$, and $\mathcal{D} = \rho^* D^*(c_0^*)/\mu$.
- Numerical values of the parameters:
  - $L \sim L_1 \sim 20, \quad \mathcal{G} \sim 10^6, \quad \mathcal{S} \sim 3{,}5 \cdot 10^5$.
  - $\mathcal{P} \sim 0 - 7{,}5 \cdot 10^4$, and $\omega \sim 0{,}15 - 3$.
- Distinguished limit:

$$L \sim L_1 >> 1, \quad \mathcal{G} >> L^2, \quad \mathcal{S} >> 1, \quad \mathcal{D} << 1,$$

and either $\omega << 1$ or $\omega \sim 1$.

THE LONG WAVE APPROXIMATION:

- $\partial_x \sim L^{-1}\partial_y << 1, \quad |v| \sim L^{-1}|u| << |u|$

$$\partial_x u + \partial_y v = 0,$$

$$\omega\partial_t u + u\partial_x u + v\partial_y u = -\partial_x p + \partial_{yy} u, \quad \partial_y p = 0 \quad \text{in } -1 < y < 0,$$

$$u = 0 \text{ at } y = -1,$$

$$\partial_y u = -\mathcal{P}\partial_x \Pi(c), \quad \omega\partial_t c + \partial_x(uc) = 0, \quad \text{at } y = 0.$$

Aditional assupmtions:

1. Free surface elevation has been neglected.

$$\text{If} \quad \mathcal{G} >> L^2 \Rightarrow |f| \sim \omega L^2/\mathcal{G} << \omega \sim |v|.$$

$$\text{Thus} \quad v = 0 \text{ at } y = 0 \Rightarrow \int_{-1}^{0} u dy$$

2. The capillary layers can be neglected, and assuming that these regions do not accumulate any significant amount of liquid,

$$u = \pm L\omega X_b'(t) \quad \text{at } y = 0, \ x = \pm L X_b(t)$$

The long wave approximation:

- $\partial_x \sim L^{-1}\partial_y << 1, \quad |v| \sim L^{-1}|u| << |u|$
- $\xi = x/L, \quad \hat{u} = u/(\omega L), \quad \hat{v} = v/(\omega L^2), \quad \hat{p} = p/(\omega L^2).$

$$\partial_\xi \hat{u} + \partial_y \hat{v} = 0,$$

$$\omega(\partial_t \hat{u} + \hat{u}\partial_\xi \hat{u} + \hat{v}\partial_y \hat{u}) = -\partial_\xi \hat{p}(\xi, t) + \partial_{yy}\hat{u} \quad \text{in } -1 < y < 0,$$

$$\hat{u} = 0 \text{ at } y = -1,$$

$$\partial_y \hat{u} = -4\hat{\mathcal{P}}\partial_\xi \Pi(c), \quad \partial_t c + \partial_\xi(\hat{u}c) = 0 \quad \text{at } y = 0,$$

$$\int_{-1}^{0} \hat{u}\, dy = 0, \quad \hat{u}(y = 0, \xi = \pm X_b(t)) = \pm X_b'(t),$$

where $\hat{\mathcal{P}} = \mathcal{P}/(4\omega L)$.

In the limit $\omega << 1$,

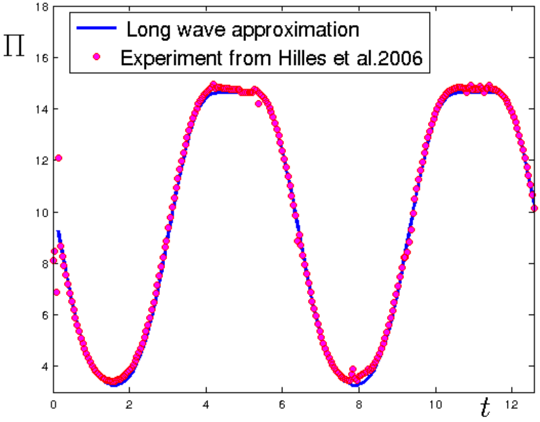
$$\partial_t c = \hat{\mathcal{P}}\partial_\xi[c\partial_\xi \Pi(c)] \quad \text{in } -X_b(t) < \xi < X_b(t)$$

$$\hat{\mathcal{P}}\partial_\xi \Pi(c) = \mp X_b'(t) \quad \text{at } \xi = \pm X_b(t).$$

1. The diffusivity comes from the combined effect of Marangoni stresses and viscous diffusion of the fluid bulk.
2. The above approximation preserves surfactant conservation and reflection symmetry ($\xi \to -\xi$).

RESULTS

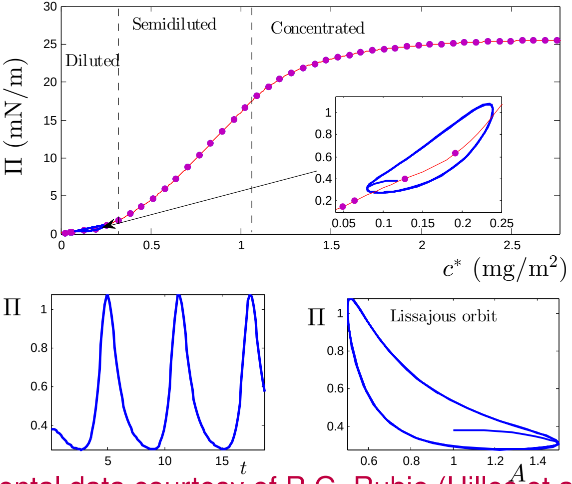
- **Initial condition:** $c_0^* = 1{,}085$.
- **Parameters:** $a = 0{,}3$, $\omega = 0{,}54$, $\hat{P} = 21{,}32$



Experimental data courtesy of R.G. Rubio (Hilles et al. 2006).

Results within diluted regime

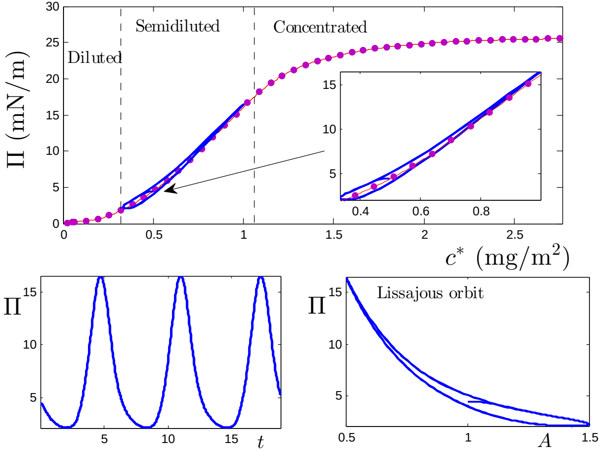
- **Initial condition:** $c_0^* = 0{,}12$.
- **Parameters:** $a = 0{,}3$, $\omega = 0{,}54$



Experimental data courtesy of R.G. Rubio (Hilles et al. 2006).

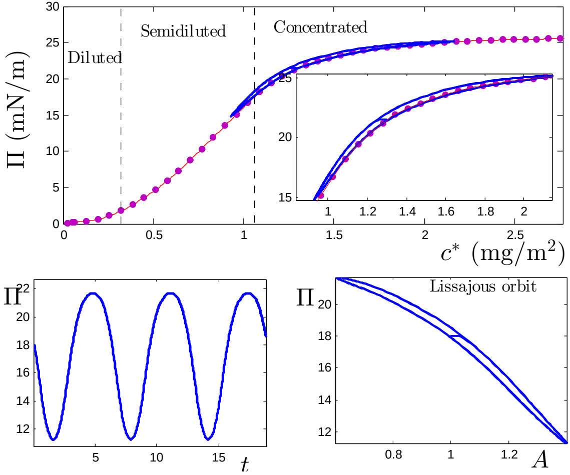
Results within semidiluted regime

- **Initial condition:** $c_0^* = 0{,}5$.
- **Parameters:** $a = 0{,}3$, $\omega = 0{,}54$



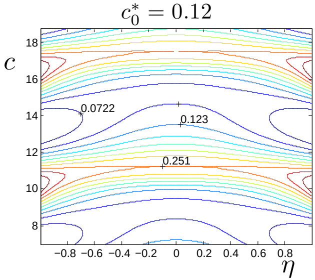
Results in semidiluted-concentrated regimes

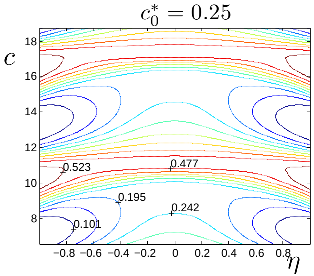
- **Initial condition:** $c_0^* = 1{,}3$.
- **Parameters:** $a = 0{,}4$, $\omega = 0{,}54$

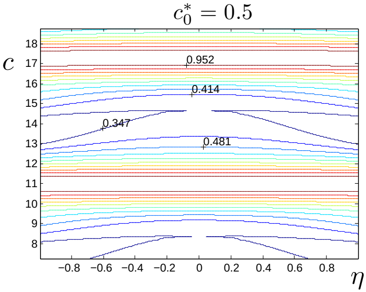


RESULTS OF CONCENTRATION FOR DIFFERENT INITIAL CONDITIONS

- **Forcing amplitude:** $a = 0{,}3$.



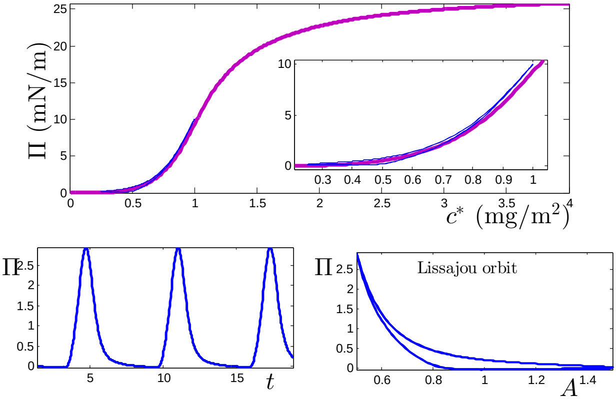




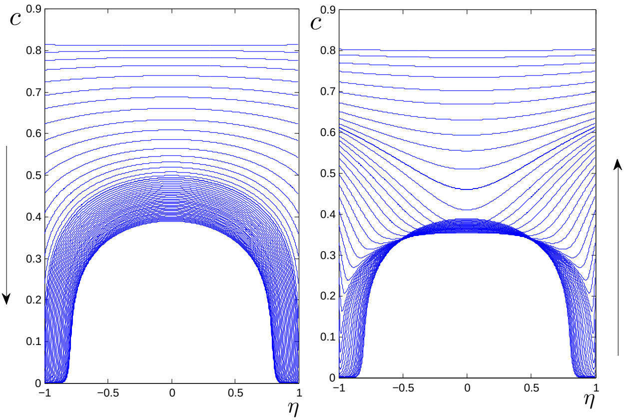
Some more interesting results for PODA

Initial condition: $c_0^* = 0{,}35$

Parameters: $a = 0{,}5$ $\omega = 0{,}54$



CONCENTRATION PROFILES VS. SPATIAL VARIABLE $\eta = \xi/(1 + a \sin t)$



- Arrows indicates the direction of increasing time.

1. A long wave approximation has been derived to describe the dynamics of polymer Langmuir monolayers compressed/expanded periodically.
2. The results indicate that the fluid dynamics should not be ignored, and may be responsible for observed irreversible dynamics.
3. Additional fluid dynamic effects could also affect the response of the system.
   - The free surface deformation.
   - The dynamics of the menisci attached to both the barriers and the plate (located in the symmetry plane) that is used to measure the surface pressure.